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(54) Aluminum oxynitride having improved optical characteristics and method of manufacture

(57) A method of preparing substantially homogeneous aluminum oxynitride powder is provided comprising the steps (a) reacting aluminum oxide with carbon black in the presence of nitrogen, (b) heating to produce a reacted powder and (c) breaking down the resulting powder into particles in a predetermined size range.

A method of preparing a durable optically transparent body from this powder is provided in which the presence of predetermined additives enhance the sintering process. Preferred dopant additives are boron, in elemental or compound form, and at least one additional element selected from the group of yttrium and lanthanum or compounds thereof.

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SPECIFICATION

Aluminium oxynitride having improved optical characteristics end method of manufacture

This invention relates to durable transparent ceramic compounds. There is a need for these compounds in applications raquiring substantial transmission and imagIng capabilities in the visibla range and the infrared range. Thesa requirements can be found in both military and commercial applications. For example, infrared transparent domes are naedad for missiles and transparent envelopes are needed In different typas of vapor lamps. Many transparent materials are not adequately durable for thesa applications, thus, the saarch has been directad towards develoing trensparent ceramics. Although many ceramic compounds satisfy the durability raquiremant, they are not transparent to a sufficient degree for these applications. For instance, alumina is a very hard material but tha mein problem is that it is not sufficiently transparant and scatters light to an excassiva degraa. An additional consideration for a candidate material is the cost of manufacturing, thus, methods that require individual processIng of thesa windows are bound to ramain an unfeasible alternative from a cost point of viaw. From this perspective, forging and hot-pressing methods are not dasirable. This leaves batch processing mathods as a desirabla feasibla alternativa end sintering lends itself to tha manufacture of a plurality of units in a single run. However, the sintering of transparent ceramics is not widely known or practiced.

Aluminum oxynitride is a promising candidate for applications raquiring multi-spactral transmission capabilities. The only known prior attempt at producing e sintared aluminum oxynitride body is found In U.S. Petent No. 4,241,000, wherein precursor powders are mixed and the sintering step is used to both react and sinter the precursor powders to produca an oxynitride body. The problem is that the resulting material is not sufficiently transparent for tha applications mentioned hereinabove.

These and other problems are solved by tha prasent invention which provides a method for producing a substantially homogeneous cubic aluminum oxynitride powder which is particularly useful for the sintering of tha powdar to produce a durabla transparent caramic window. It was found thet starting with a substantially homogeneous powder of aluminum oxynitrida es prepared by the presant invention and using specific additivas laads to an adequataly transparant window In both the visible and infrared range.

This invention provides for a method of preparing homogeneous aluminum oxynitride comprising the steps of introducing aluminum oxide powder and carbon black in a reaction chamber, providing nitrogen in said chamber, and heating said chambar to react seid powder and gas for producing a reacted powder substantially comprising aluminum oxynitride. The reactad powder may also comprise up to 15 weight percant of aluminum oxide and aluminum nitrida such that the ratio of aluminum oxide to aluminum nitride is within tha composition range of cubic aluminum oxynitride.

This invention further provides for a method of producing transparant sinterad aluminum oxynitride bodies comprising the steps of preparing a mixture of eluminum oxide and carbon black, reacting the mixture in the presence of nitrogan and a tamperatura in tha range of 1550—1850°C, forming a pressed green body of predetermined shape from seid mixture, placing said green body in a sintaring chamber, providing doping additions in said chamber, said additives comprising one or more elements from the group of yttrium and lanthanum, or compounds thereof, and sintering said grean body at a temperature higher than 1900°C but lower than the solidus temperature of aluminum oxynitride. Preferably, the dopants are in a vapor phasa during a portion of said sintering stap and vapor transport to and diffuse throughout said body. The doping additives comprise not more than 0.5 weight parcent of tha weight of the green body. The preferred starting mixture has a carbon contant in the range of 5.4—7.1 weight percent. Preferably, tha reacted mixture is broken up in particles of size in the range of 0.5 to 5 microns, and the reacted mixture is heated In air or oxygen to remova any orgainc contaminants that might be present.

Additionelly, this invention provides a cubic aluminum oxynitrida body heving a density of at leest 99% of theoretical density, an in-line transmission of at least 50% in the wavelength range of 0.3—5 microns, and preferably an image resolution of 1 mrad or less.

The present Invention produces a substantially homogenaous cubic aluminum oxynitride powder by reacting gamma-aluminum oxide with carbon in a nitrogen atmosphere. More specifically, and preferably, aluminum oxide (alumina) and carbon black are dry mixed, for instance, in a Petterson-Kelly twin-shell blender for times up to two hours. Preferably, tha aluminum oxide has a purity of at least 99.98% and an average particle siza of 0.06 microns, and the carbon black has a purity of no less than 97.6% with 2.4% volatile content and an average particle size of 0.027 microns. The carbon contant of the mixture can range from 5.4 to 7.1 weight parcent. A preferred mixture comprises 5.6 weight percent carbon black and 94.4 weight percent aluminum oxide. The aluminum oxide/carbon mixture is preferably placed in an alumina crucible and reacted in an atmosphere of flowing nitrogen at temperatures from 1550°C to 1850°C for up to two hours at the maximum temperature. The preferred heat treatment is in two steps. In the first step, a temperature of approximately 1550°C is used for approximately one hour, whereby, for an appropriate ratio of alumina to carbon, the temperature unstable gamma-aluminum oxide is only partially reactad with carbon and nitrogen to form both alpha-aluminum oxide and aluminum nitride. A one hour soak at 1550°C is sufficient to

convert the proper amount of Al_2O_3 to AlN. In the second step, a temperature of 1750°C or up to the solidus temperature of aluminum oxynitride (2140°C), is used for approximately 40 minutes, whereby alpha-aluminum oxide and aluminum nitride combine to form cubic aluminum oxynitride.

The reacted material resulting from the heet treatment is composed primarily of cubic aluminum oxynitride, but may also contain alumina and/or aluminum nitride in amounts of up to 15 weight percent such that the ratio of elumlnum oxide to aluminum nitride is within the composition range of cubic aluminum oxynitride. The amounts of alumina and aluminum nitride can be controlled by the heat treatment and the amount of aluminum nitride produced in the first heating step which in turn depends on the emount of cerbon in the starting mixture.

For a first step utilizing the preferred one hour soak at 1550°C, except for Sample 5 which was treated at 1620°C, Table I illustrates the effect of using different amounts of carbon in the starting mixture end of different temperetures during the second step of the heat treetment.

Table I

Sample	*Weight % carbon*	*Temp. (°C)*	*Time (mins)*	*% AlN*	*% Al_2O_3*	*% ALON*
1	5.6	1750	40	3.2	10.0	86.8
2	7.1	1750	40	4.0	0	96.0
3	6.5	1750	40	1.88	0	98.12
4	5.9	1750	40	0.85	0	99.15
5	5.6	1820	40	Trace	Trace	99.9+

The preferred heet treatment produces e resulting composition comprising substantially 100% aluminum oxynitride end corresponds to Semple 5. An alternete preferred resulting composition is that of Semple 1. The resulting aluminum oxynitride powder consists of agglomerated particles which are easily broken apart during ball milling to particles ranging in size from 0.5 to 5 microns.

The reacted materiel is ball milled in polyurethane or rubber lined mills using methanol es a milling fluid and high alumina grinding balls. Milling time is 16 hours. The milled powder is passed through a 400 mesh and is dried at 65°C for up to 24 hours. After drying, the powder is heated in air to 600°C for 2 hours to remove orgenic conteminants.

Sintering aids are now added in the form of small amounts of preselected doping additives up to 0.5 weight percent of the aluminum oxynitride powder. The edditive mey also comprise en element selected from the group of yttrium and lanthanum, or compounds thereof. Other elements of the lanthanide series may similerly be used. Preferebly, the oxides of the elements selected are used. A combination of the doping additives may also be used as long as the total amount of edditives does not exceed 0.50 weight percent. A preferred combination comprises 0.08 weight percent yttrium oxide (Y_2O_3) and 0.02 weight percent lenthanum oxide (La_2O_3). Alternetively, the doping edditives mey be added during the ball milling of the aluminum oxynitride powder.

The additive-containing aluminum oxynitride powder is placed in rubber molds having predetermined shepes and is isostatically pressed at pressures greater than 15,000 psi to produce green bodies to be used in sintering. The fabricated green bodes are set in containers in the sintering chamber. The containers are composed either entlrely of boron nitride or partly of boron nitride and partly of molybdenum metal. Sintering is then performed in a stagnant atmosphere of nitrogen at 0—5 psig. To obtain substantially transparent material, sintering temperatures ere higher than 1900°C, but lower than the solidus temperature of aluminum oxynitride which is epproximately 2140°C. Sintering is preferebly carried out for a minimum of 24 hours end a maximum of 48 hours.

Table II

Sample	*Y_2O_3*	*La_2O_3*	*Temp. °C*	*Time h*	*% in-line transmiss. @ 24 microns*	*(mm) Thickness*	*% Density*	*Optical resolution*
1	none	none	1930	23	opaque	1.7	98	—
2	0.08	0.02	1930	1	5	0.82	98+	—
3	0.08	0.02	1930	24	80	1.45	99+	<1 mrad
4	0.25	none	1930	48	53	1.35	99+	<1 mrad
5	0.08	0.02	1730	3	opaque	1.5	—	—
6	0.08	0.02	1910	8	5	0.8	98	—

Table II shows to some extent the effect of additives, time and temperature on the resultant transparency of the eluminum oxynitride. The density was measured by the Archimedes method, the in-line transmission wes measured with e Perkin-Elmer 457 Grating Infrared Spectrophotometer, and the resolving angle was measured by using the Standard USAF 1951 Resolution Test Pattern. The temperatures are accurate to within 10°C. A temperature of 1900°C is the minimum temperature

found to consistently produce a transparent material given the proper amount of Y_2O_3 and/or La_2O_3. The best amount of additive is in the minimum amount needed to produce a liquid phase at the grain boundaries initially yet not be present as a second phase after sintering. Although 0.1 weight percent produced the best results, smaller trace amounts as low as 0.05 weight percent may be used, provided that a liquid phase is formed at or near 1900°C which promotes rapid densification and pore removal. This liquid phase disappears with Y and La going into solid solution with the aluminum oxynitride. This process of liquid phase sintering is thought to be present at the sintering temperature early in the sintering process. After this, solid state diffusion is the means by which the remaining porosity is eliminated and a substantial transparency is achieved. Elimination of porosity by solid state diffusion is a much slower means of pore elimination so longer times are needed, 24 hours being the minimum preferred duration. This is confirmed by Samples 2 and 6, wherein, even though an adequate amount of additives was used, the samples remain translucent because the duration of the sintering step was limited to 1 and 8 hours, respectively.

It should be understood that the additives discussed hereinabove need not be mixed in with the aluminum oxynitride powder prior to sintering nor do they need to be placed in direct contact with the green body. Again, it is sufficient that the selected additive be available within the sintering chamber for the doping of the aluminum oxynitride. Indeed an unexpected improvement in the transparency of sintered aluminum oxynitride was discovered after sintering a green body, composed strictly of aluminum oxynitride powders, along with an adjacent green body containing yttrium oxide on a boron nitride platform. Thus, this invention is considered to encompass other methods of introducing the additives in the sintering chamber to produce in situ vapor doping of the aluminum oxynitride compact.

An explanation of in situ vapor doping by the presence of specific additives for the enhancement of the sintering is believed to be as follows. At sintering temperatures, the mixture of aluminum oxynitride has a significantly high vapor pressure of Al_xO_y gas species. The Al_xO_y gas reacts with nearby boron nitride present in the container to produce B_2O_3 gas and/or $AlBO_2$ gas plus AlN solid. The B_2O_3 and/or $AlBO_2$ vapors transport to and react with aluminum oxynitride to produce a liquid phase at grain boundaries which enhances the early stages of sintering. In the case yttrium oxide is used as the additive, the B_2O_3 also interacts with yttrium doped aluminum oxynitride or pure Y_2O_3 to produce YBO_2 gas. The YBO_2 vapor transports to the aluminum oxynitride and dopes it with the boron and yttrium. In the case of other elements being used as additives, the B_2O_3 similarly reacts to provide a corresponding vapor doping of aluminum oxynitride. It is believed that this additive doping aids the final stages of sintering by causing either solute drag or second phase precipitates to pin grain boundaries and thus preventing excessive grain growth which might otherwise trap pores within the grains.

An alternate explanation is that the yttrium, or components thereof, cause the formation of a liquid phase. This liquid phase promotes rapid densification and significant pore removal in the early stages of sintering so that during the final stages of sintering there is less porosity to be eliminated and high density and transparency are achieved. In this mechanism, boron is necessary only for the transport of yttrium to the aluminum oxynitride.

The method of the present invention avoids many of the problems normally associated with the preparation of aluminum oxynitride by mixing and reacting aluminum oxide and aluminum nitride, such as the varying purity levels, large particle sizes and wide size distribution range of commercially available aluminum nitride, the long reaction times required to form aluminum oxynitride, and the long milling times required to reduce the particle size, which in turn increase the inorganic impurity content of the aluminum oxynitride. Additionally, the present method reduces the cost of manufacturing by avoiding the use of the more expensive aluminum nitride as a starting ingredient, by requiring shorter reaction times to form aluminum oxynitride, and by requiring less milling time to achieve a homogeneous sinterable powder of suitable particle size. The aluminum oxynitride powder prepared by the present method also improves the reproducibility of the sintering process and improves the transparency of the sintered product.

Claims

1. A method of preparing homogeneous aluminum oxynitride comprising the steps of:
introducing aluminum oxide powder and carbon black into a reaction chamber;
providing nitrogen in said chamber; and
heating said chamber to react said powders and gas for producing a reacted powder substantially comprising aluminum oxynitride.

2. A method according to claim 1 wherein:
said reacted powder comprises up to 15 weight percent of aluminum oxide and aluminum nitride such that the ratio of aluminum oxide to aluminum nitride is within the composition range of cubic aluminum oxynitride.

3. A method according to claim 1 or claim 2 wherein:
said aluminum oxide and carbon black are introduced as a thoroughly mixed mixture.

4. A method according to any one of claims 1 to 3 wherein:
the carbon content of said mixture is in the range of 5.4 to 7.1 weight percent.

5. A method according to any one of claims 1 to 4 wherein:

said aluminum oxide hes a purity of 99.98% and an average particle size of approximately 0.06 microns, and said carbon black has a purity of 97.6% and an average particle size of approximately 0.027 microns.

6. A method according to any one of clalms 1 to 5 wherein:

said chamber is heated to a temperature in the range of 1550—1850°C.

7. A method according to claim 6 whereln said heating step comprises the steps of:

first heating said chamber to a temperature in the lower end of said temperature range to convert the temperature unstable gamma aluminum oxide present in the mixture into the temperature stable alpha aluminum oxide; and

then heating said chamber to a temperature in the upper end of said temperature range to react said converted mixture of powder with said nitrogen gas to produce aluminum oxynitride.

8. A method according to claim 7 wherein:

said chamber Is first heated to a temperature of approximately 1550°C for approximately an hour and then to a tempereture of 1750°C for approximately 40 minutes.

9. A method according to claim 7 wherein:

seid chamber is first heated to a temperature of approximately 1620°C for approximately one hour and then to a temperature of 1820°C for approximately 40 mlnutes.

10. A method accordlng to any one of claims 1 to 9 comprising the additional step of:

milling said reacted powder to produce particles of size In the range of 0.5 to 5 microns.

11. A method according to any one of clalms 1 to 10 comprising the step of:

heating sald powder in air until any organic conteminants present in the mixture are substantially removed.

12. A method of preparlng homogeneous aluminum oxynitride comprising the step of:

preparing a mixture of aluminum oxide and carbon black, the carbon content of said mixture being in the range of 5.4—7.1 welght percent;

reacting in a flowing nltrogen atmosphere said mixture first at a temperature of approximately 1550°C for one hour, and then at a temperature of at least 1750°C for 40 minutes;

ball milling the reacted mixture with alumina grinding balls in methanol; and

filtering said milled powder through a 400 mesh.

13. A method according to claim 12 further comprising the steps of:

drying said filtered powder; and

heatlng sald powder in alr to remove any organic contaminants that might be present.

14. A method of producing transparent sintered aluminum oxynitrlde bodies comprising the steps of:

preparing a mixture of aluminum oxide end carbon black;

reacting said mlxture in the presence of nitrogen and at a temperature In the range of 1550—1850°C;

forming a pressed green body of predetermined shape from said mixture;

placing said green body in a sintaring chamber;

providing doplng additives in said chamber, said additives comprising one or more elements from phe group of yttrium and lenthenum or compounds thereof; and

sintering sald green body in a nitrogan atmosphere at a temperature higher than 1900°C but lower than the solidus tempereture of aluminum oxynitride.

15. A method according to claim 14 wherein:

the carbon content of said mixture is In the range of 5.4—7.1 weight percent.

16. A method according to claim 14 or claim 15 wherein:

said dopants are in a vepor phase during a portion of said sintering step.

17. A method according to any one of clalms 14 to 16 whereln:

in said sintering step, the dopants transport to and diffuse throughout said body.

18. A method according to any one of claims 14 to 17 wherein:

said dopants produce a llquid phase at grain boundarles during said sintering step.

19. A method according to any one of claims 14 to 18 wherein:

said doping additives are mixed in with said mixture.

20. A method according to any one of claims 14 to 19 wherein:

said doping edditives comprise not more than 0.5 weight percent of said mixture.

21. A method according to any one of claims 14 to 20 further comprising the steps of:

breaking up the reacted mixture in perticles of size in the range of 0.5 to 5 microns; and

heating said reacted mixture to remove organic contaminants.

22. A cubic aluminum oxynitride body having a density of at least 99% of theoretical density, an in-line transmission of at least 50% in the wavelength range of 0.3—5 microns and a resolving angle of 1 mrad or less.

23. A doped aluminum oxynitride body having a density of at least 99% of theoretical density an in-line transmissivity of at least 50% in the 0.3—5 micron wavelength range.

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